

# FUNCTIONALIZED, STRUCTURALLY MODIFIED SILICAS

## Introduction and Background

The present invention relates to functionalized, structurally modified silicas, a process for their preparation and their use.

- 5 It is known to react silicon dioxide obtained by flame hydrolysis and with a surface area of 40 to 200 m<sup>2</sup>/g with 3-methacryloxypropyl-trimethoxysilane. The resulting silicon dioxide is then coated with a further shell of (meth)acrylate polymers and subsequently employed in dental compositions (EP 0 142 784 A1).

- It is known to silanize a silica with hexamethyldisilazane and then to destructure or to  
10 compact it by mechanical effects (EP 0 808 880 A2).

The known silica has the disadvantage that it can be incorporated into coating systems only with difficulty or not at all because its thickening effect is too high.

It is therefore an object of the present invention to develop a functionalized, structurally modified silica which does not have this disadvantage.

## 15 Summary of the Invention

The above and other objects of the present invention can be achieved by functionalized, structurally modified silicas, characterized by functional groups fixed on the surface, the groups being 3-methacryloxypropylsilyl and/or glycidyloxypropylsilyl, with the following physico-chemical characteristic data:

20	BET surface area	m <sup>2</sup> /g	25 - 380
	Particle size	nm	6 - 45
	Tamped density	g/l	50 - 400
	pH		3 - 10
	Carbon content	%	0.1 - 15
25	DBP (dibutylphthalate) number	%	<200

The present invention also provides a process for the preparation of the functionalized, structurally modified silicas according to the invention, which is characterized in that a

silica is sprayed optionally first with water or dilute acid and then with a surface modification reagent or a mixture of several surface modification reagents in a suitable mixing vessel, with intensive mixing, the components are optionally re-mixed for 15 to 30 minutes and heat-treated at a temperature of 100 to 400 °C over a period of 1 to 6 h, 5 and the functionalized silica is then destructured/compacted by mechanical effects and optionally re-ground in a mill.

According to the invention, a ball mill, for example, can be employed for the destructuring. The re-grinding can be carried out, for example, by means of an air jet mill or pinned disc mill.

- 10 A silica prepared pyrogenically by the route of flame hydrolysis of  $\text{SiCl}_4$  can preferably be employed as the silica. Such pyrogenic silicas are known from Ullmanns Enzyklopädie der technischen Chemie [Ullmanns Encyclopaedia of Industrial Chemistry], 4th edition, volume 21, page 464 (1982).

In a preferred embodiment of the invention, a pyrogenic silica with a surface area of 15 approx. 200  $\text{m}^2/\text{g}$  can be reacted (Aerosil® 200).

Monomeric substances, such as the organo alkoxysilanes, e.g., 3-methacryloxypropyl-trialkoxysilane and/or glycidylloxypropyltrialkoxysilane, wherein alkoxy can be methoxy, ethoxy and/or propoxy, can be employed as the surface modification reagent.

The amount of silane can be metered in with respect to the silica such that no excess 20 results. The excess silane can optionally be removed during the heat treatment.

The silica according to the invention can be employed in radiation-curing coatings containing a binder vehicle, for example UV coatings.

The scratch resistance of the surfaces is advantageously improved by the use of the silica according to the invention.

- 25 The silicas according to the invention have only a slight influence on the rheology of the coating system. Because the viscosity of the coating is increased only slightly, relatively large amounts of silica can be incorporated into the coating.

The functional groups on the silica can react with organic compounds.

According to the invention, the pyrogenically prepared silicas according to table 1 can be employed as the silica for the silanization.

Table 1

Physico-chemical data of AEROSIL

Test method		AEROSIL 90	AEROSIL 130	AEROSIL 150	AEROSIL 200	AEROSIL 300	AEROSIL 380	AEROSIL OX 50	AEROSIL TT 600
Behaviour towards water		hydrophilic							
Appearance		loose white powder							
BET surface area <sup>1)</sup>	m <sup>2</sup> /g	90±15	130±25	150±15	200±25	300±30	380±30	50±15	200±50
Average primary particle size	nm	20	16	14	12	7	7	40	40
Tamped density approx. values <sup>2)</sup>	g/l	80	50	50	50	50	50	130	60
Compacted goods (added "V")	g/l	120	120	120	120	120	120		
VV goods (added "VV") <sup>12)</sup>	g/l			50/75	50/75	50/75			
Loss on drying <sup>3)</sup> (2 hours at 105°C) on leaving supply works	%	<1.0	<1.5	<0.5 <sup>9)</sup>	<1.5	<1.5	<2.0	<1.5	<2.5
Loss on ignition <sup>4)</sup> (2 hours at 1000°C)	%	<1	<1	<1	<1	<2	<2.5	<1	<2.5
PH <sup>5)</sup>		3.7-4.7	3.7-4.7	3.7-4.7	3.7-4.7	3.7-4.7	3.7-4.7	3.8-4.8	3.6-4.5
SiO <sub>2</sub> <sup>8)</sup>	%	>99.8	>99.8	>99.8	>99.8	>99.8	>99.8	>99.8	>99.8
Al <sub>2</sub> O <sub>3</sub> <sup>8)</sup>	%	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.08	<0.05
Fe <sub>2</sub> O <sub>3</sub> <sup>8)</sup>	%	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.01	<0.003
TiO <sub>2</sub> <sup>8)</sup>	%	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03
HCl <sup>8)10)</sup>	%	<0.025	<0.025	<0.025	<0.025	<0.025	<0.025	<0.025	<0.025
Sieve residue <sup>9)</sup> (Mocker method, 45 µm)	%	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.2	<0.05
Drum size (net) <sup>11)</sup>	kg	10	10	10	10	10	10	10	10

1) in accordance with DIN 66131 2) in accordance with DIN ISO 787/XI, JIS K 5101/18 (not sieved) 3) in accordance with DIN ISO 787/II, ASTM D 280, JIS K 5101/21 4) in accordance with DIN 55921, ASTM D 1208, JIS K 5101/23 5) in accordance with DIN ISO 787/IX, ASTM D 1208, JIS K 5101/24 6) in accordance with DIN ISO 787/XVIII, JIS K 5101/20	7) based on the substance dried for 2 hours at 105 °C 8) based on the substance ignited for 2 hours at 1000 °C 9) special packaging protecting against moisture 10) HCl content is a constituent of the loss on ignition 11) V goods are supplied in sacks of 20 kg 12) VV goods are currently supplied only from the Rheinfelden works
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### Example 1

5 Aerosil® 200 is mixed with 4 parts water and 18 parts 3-trimethoxysilyl-propyl methacrylate and the mixture is heat-treated at 140 °C under an inert gas. The silanized silica is then compacted to approx. 250 g/l on a continuously operating vertical ball mill. The silica obtained has the following properties:

BET [m <sup>2</sup> /g]	138
Tamped density [g/l]	242
pH	4.6
C content	5.7
Loss on drying [%]	0.6
Loss on ignition [%]	8.9
DBP number [%]	122

Experiments with AEROSIL R 8200 and silica according to example 1 in UV-curing binders:

Experiment 1:

5 AEROSIL® is stirred into the binder 1 (ethoxylated pentaerytholtetraacrylate) Sartomer SR 494, Cray Valley, with a dissolver and then predispersed for 5 min at 3000 rpm (disc Ø 45 mm). The mixture is dispersed in a laboratory bead mill for 15 min (AEROSIL® 8200) or

20 min (silica according to example 1) at 2500 rpm and a pump output of 60 %  
10 (AEROSIL® 8200) or 40 % (silica according to example 1). 1 mm glass beads are used as the beads. The dispersing quality is checked with a grindometer, 25 µm; in accordance with DIN ISO 1524. It must be smaller than 10 µm.

3 % photoinitiator is stirred into the coating. Application is carried out with the aid of a spiral doctor blade (amount applied 36 µm) on black-lacquered metal sheets. Curing is  
15 carried out with a UV unit (current uptake of the UV lamp (mercury vapour lamp) 7.5 - 10 mA, belt speed 10 m/min, irradiation intensity 1 W/cm).

Experiment 2:

AEROSIL® is stirred into the binder 2 (epoxyacrylate) with a dissolver and then predispersed for 5 min at 3000 rpm (disc Ø 45 mm). The mixture is dispersed in a  
20 laboratory bead mill for 15 min at 2500 rpm and a pump output of 70 % (AEROSIL® 8200) or 40 % (silica according to example 1). 1 mm glass beads are used as the beads. The dispersing quality is checked with a grindometer, 25 µm, in accordance with DIN ISO 1524. It must be smaller than 10 µm.

3 % photoinitiator is stirred into the coating. Application is carried out with the aid of a  
25 spiral doctor blade (amount applied 36 µm) on black-lacquered metal sheets. Curing is carried out with a UV unit (current uptake of the UV lamp (mercury vapour lamp) 7.5 - 10 mA, belt speed 10 m/min, irradiation intensity 1 W/cm).

Incorporation of silica according to R 8200:

Marked foaming is already to be observed during the predispersing (10 % AEROSIL® based on binder solids). The viscosity also increases sharply due to the AEROSIL® 8200 (see table 1). The foam is intensified during the dispersing in the bead mill. Application of the coating with a smooth, bubble-free surface is not possible.

5 Incorporation of silica according to example 1:

Slight foaming is to be observed during the predispersing (10 % VP based on binder solids), the foam having disappeared after the bead mill dispersing. After application and crosslinking of the film, a smooth, high-gloss surface results.

Table 2

10 Grindometer values, Brookfield viscosities:

	Grindometer value [μm]	Viscosity [mPa s]		Pseudo- plasticity 6/60
		6 rpm	60 rpm	
<b>binder 1</b>	-	160	158	1.0
<b>binder 1 + Aerosil R 8200</b>	<10	35,900	6,830	5.2
<b>binder 1 + silica according to example 1</b>	<10	451	389	1.1
<b>binder 2</b>	-	481	468	1.0
<b>binder 2+ Aerosil R 8200</b>	<10	53,300	10,000	5.3
<b>binder 2 + silica according to example 1</b>	<10	1,000	950	1.1

Scratching experiments:

The metal sheets are scoured with a quartz/water slurry (100 g water + 1 g Marlon A 350, 0.25 % + 5 g Sikron F500) with 100 strokes with the aid of a scouring and washing resistance testing machine (Erichsen). The shine before and 10 min after scouring is determined with a reflectometer (20 ° incident angle).

Table 3

Reflectometer values before and after scratching:

	20 ° reflectometer value		Residual shine [%]
	before	after	
<b>binder 1</b>	82.0	50.0	61.0
<b>binder 1 + silica according to example 1</b>	80.5	65.2	81.0
<b>binder 2</b>	89.6	46.5	51.9
<b>binder 2 + silica according to example 1</b>	87.8	67.4	76.8

Further variations and modifications of the foregoing will be apparent to those skilled in the art and are intended to be encompassed by the claims appended hereto.

European application EP 00 122 955.8 is relied on and incorporated herein by reference.